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Exciton and Hole-Transfer Dynamics in Polymer: Fullerene Blends

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Abstract. Ultrafast hole transfer dynamics from fullerene derivative to polymer in bulk heterojunction blends are studied with visible-pump – IR-probe spectroscopy. The hole transfer process is found to occur in 50/300 fs next to the interface, while a longer 15-ps time is attributed to exciton diffusion towards interface in PC₇₁BM domains. High polaron generation efficiency in P3HT blends indicates excellent intercalation between the polymer and the fullerene even at highest PC₇₁BM concentration thereby yielding a valuable information on the blend morphology.

A heterojunction of two organic materials is widely used in photosynthetic systems, photocatalytic reactions, organic optoelectronics, and plastic photovoltaics. In the latter devices, the role of the donor is played by a great variety of conjugated molecules, including the more recent narrow-bandgap polymers, while the overwhelming majority of cases utilize the same class of molecules as acceptor: the (soluble) fullerene derivatives, e.g. PCBM. In describing the functionality of these photovoltaic systems one usually considers the process in which an exciton in the donor material dissociates by transfer of an electron to the acceptor material. This is, however, only half the story. It has been shown that the mirror process in which charges are generated by dissociation of an acceptor exciton is very efficient as well [1]. Although the importance of hole transfer was recognised only recently, the first devices functioning primarily on hole transfer have already been demonstrated [2].

Charge generation processes are but one of the processes which determine the eventual efficiency of devices. For the efficiency, one of the most important parameters is the morphology of the bulk heterojunction architecture. In an ideal morphology, the interfacial region is maximized for the most efficient exciton dissociation at the interface. At the same time, the ideal morphology would optimize the percolation pathways of the generated charges toward the contacts.

Here we report on an ultrafast photophysics study of PC₇₁BM based photovoltaic blends addressing ultrafast hole transfer dynamics and the associated material morphology. Our results demonstrate that visible pump – IR probe spectroscopy is not only a powerful tool for studying charge dynamics, but also allows extracting important information on the morphology of the blends, which otherwise is notoriously difficult to obtain.

We used PC₇₁BM as hole donor material, chosen for its substantial absorption in the visible range. As hole acceptor materials MDMO-PPV and rr-P3HT were used, where the former has a purely amorphous structure and the latter typically possesses both disordered as well as crystalline domains. In our experiments we photo-excite the fullerene derivative at the red absorption flank where the fullerene absorbs significantly stronger than the polymer (630 nm for MDMO-PPV:PC₇₁BM and 680 nm for P3HT:PC₇₁BM based blends), while monitoring the arrival of

a hole in the polymer domain through the appearance of the typical polaron IR absorption bands [1,3] using a 0.41 eV probe pulse (Figure 1a).

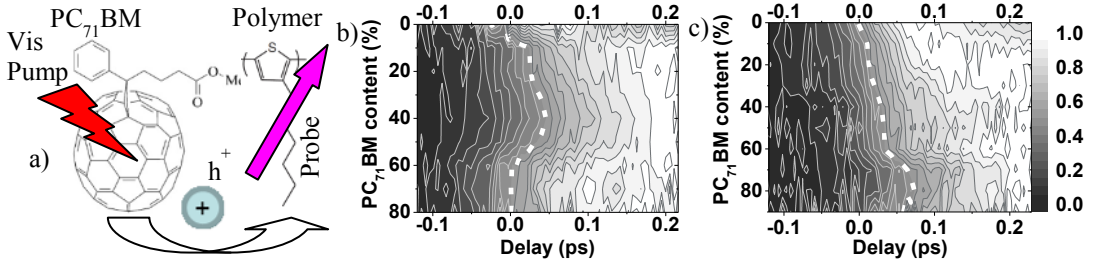


Fig.1. The schematics of photophysical processes following fullerene excitation (a). Polaron response as a function of time at different fullerene weight content for MDMO-PPV:PC₇₁BM (b) and P3HT:PC₇₁BM (c). The greyscale scheme shown on the right represents induced absorption of each transient normalized to 1. Contour lines are drawn with 5% step of maximal amplitude. Dashed curves show the delay where half maximum amplitude is reached.

Figures 1b,c present short-time isotropic transients for both polymers at different PC₇₁BM concentrations. At low PC₇₁BM concentration, the response originates mostly from direct excitation of the polymer while at high concentrations this contribution is overwhelmed by the PC₇₁BM excitation. For both polymers, the signal rise becomes more delayed with increasing PC₇₁BM concentration (white curves in Figure 1b,c). This retardation is assigned to the finite time needed for charge generation through hole transfer at the interface. The main difference between the two polymers is that for MDMO-PPV-based blends the retardation is levelled-off at ~30% of PC₇₁BM and even returns to smaller delay at the highest concentrations, while for the P3HT-based blends a continuously increasing delay is observed up to the highest concentrations.

To further disentangle the contributions of electron transfer (direct polymer excitation) and hole transfer (PC₇₁BM excitation), we monitored the IR transmission anisotropy after photoexcitation. The anisotropy for both polymers is presented in Figure 2a at 0.5 ps delay as a function of PC₇₁BM concentration. For low concentration, when primarily the polymer is excited, the anisotropy level is high demonstrating the correlation of the transient dipole moment directions at excitation and probe frequencies. At high concentrations, the fullerene excitation prevails; hence there should be no correlation between the two, as observed.

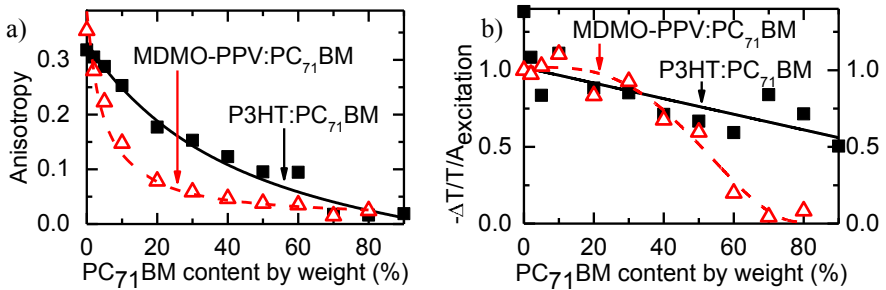


Fig. 2. Anisotropy at 0.5 ps delay (a) and maximal polaron generation efficiency (i.e. transmission changes normalized on the number of photons absorbed) – (b) as functions of fullerene content.

For obtaining the timescales involved, we performed global fitting of all isotropic and anisotropic transients with a combination of ingrowing and decaying exponents, resulting in ultrafast ingrowing components with time constants 50 fs and 300 fs, similar to our previous observation [1]. The 50 fs time scale is too short to allow any exciton diffusion in the fullerene domain, and its contribution appears with addition of even the smallest amount of PC₇₁BM. Therefore, we attribute this time to the hole transfer time of the exciton at the fullerene-polymer interface. The longer time scale appears

only at higher (5% for MDMO-PPV and 20% for P3HT) concentrations and is therefore likely to be short-length scale (within 1-2 molecules) exciton hopping. Alternatively it could be hole transfer from delocalised hot excitations originating from PC₇₁BM nanocrystals [4,5]. Therefore effectively hole is transferred over larger distance and obviously is more delayed.

To strengthen these assignments, Figure 2b shows the polaron generation efficiency for different blends. The general trend is that the efficiency decreases with increasing PC₇₁BM content. This is consistent with the formation of larger-scale domains in the blends thereby changing the ratio between interfacial and bulk regions, and hence the fraction of excitons which can charge separate (Figure 3). However, the details are strikingly different: for MDMO-PPV the efficiency remains almost constant up to 40% and then rapidly decreases to zero. This behaviour is consistent with an explosive growth of the fullerene domain size at higher concentrations [1]. AFM studies revealed that MDMO-PPV blends with 50% and 60% of PC₇₁BM form fullerene domains with size difference by a factor of 2: ~150 nm and ~350 nm respectively. This also explains the decreased retardation of the transients at large PC₇₁BM concentrations (Figure 1b): the excitons cannot escape large PC₇₁BM domains, and the electron transfer from the polymer becomes the dominant contribution.

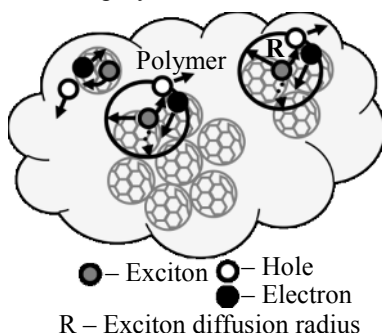


Fig. 3. Schematic representation of photoinduced processes after fullerene excitation.

In contrast to MDMO-PPV, in P3HT-based blends the efficiency still remains relatively high even at 90% of PC₇₁BM (Figure 2b) indicating reasonably good intermixing between polymer and fullerene with polymer chains intertwined among fullerene domains with distances of ~150 nm referring to MDMO-PPV blends. An additional confirmation for this conclusion is found in the appearance of a 15 ps ingrowing component in the long-delay transients (not shown) originating from exciton diffusion within fullerene domains towards the interface.

In conclusion, our results show – next to the 50 fs hole transfer time observed – that P3HT/PC₇₁BM blends possess much smaller bulk domains than the MDMO-PPV/PC₇₁BM blends, leading to an interface/bulk ratio which is more favourable for charge generation in the former case. The technique employed herein is especially useful when more traditional methods to obtain information on morphology meet substantial experimental challenges, which is in particular true for “on the fly” characterisation of the working devices.

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